

## Liquid-Liquid Phase Transition in the ST2 Model of Water: Evidence from Simulations

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Recently Limmer and Chandler argued that the liquid-liquid transition in the ST2 model of water (modified to take into account long-ranged electrostatic interactions) is a solid-liquid transition based on a free energy surface calculated using umbrella sampling techniques [Limmer and Chandler, *J. Chem. Phys.* **135**, 134503(2011)]. In order to understand the strong disagreement between the Limmer-Chandler claim and a considerable body of previous work on the subject, we have investigated the existence of the liquid-liquid transition in the supercooled region of the ST2 model of water comprehensively through a combination of state-of-the-art simulation techniques. We performed umbrella sampling *NPT* Monte Carlo simulations and computed free energy surface as a function of density and a bond-orientational order parameter,  $Q_6$ , that is able to distinguish crystalline from disordered phases [Paul J. Steinhardt, David R. Nelson, Marco Ronchetti, *Phys. Rev. B*, **28**, 784(1983)]. Contrary to Limmer and Chandler's assertion,, according to which there is a single liquid basin in the free energy landscape, we found two liquid basins at  $T = 228.6\text{K}$  and  $P = 2.2\text{Kbar}$  which supports the conclusions of our previous work [Y. Liu, A. Z. Panagiotopoulos and P. G. Debenedetti, *J. Chem. Phys.*, **131**, 104508(2009)], and provides further evidence for the existence of the low density liquid in this model. Our results are also in agreement with a recent study by Sciortino et al. [*Phys. Chem. Chem. Phys.*, **13**, 19759 (2011)]. Furthermore, at the same thermodynamic condition mentioned above, we found that the system fluctuates back and forth between LDL and HDL in *NPT* ensemble Molecular Dynamics simulations. An analysis of crystal nuclei lifetime and dynamics in the low-density liquid phase via the *NVT* ensemble Monte Carlo simulations indicates that the crystalline nuclei, which are easily formed and dissolve, do not grow in size either over time or when the system size is increased by a factor of 8, confirming that the system is clearly amorphous, with diffusion coefficient about  $0.6 \times 10^{-7} \text{ cm}^2/\text{s}$  at  $T = 228.6\text{K}$  and  $\rho = 0.92\text{g/cc}$ . A scaling of  $Q_6$  with respect to  $N^{-1/2}$  at this condition proves that  $Q_6$  vanishes in the thermodynamic limit, which also demonstrates liquid behavior. In summary, we have obtained sufficient and robust computational evidence in support of the existence of the liquid-liquid transition in the ST2 model of water, which is distinct from the crystal-liquid transition.